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MARAGING STEEL WITH SUPERIOR STRESS CORROSION CRACK RESISTANCE
[耐応力腐食割れ性にすぐれたマルエージング鋼]

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(54) Title of the Invention **MARAGING STEEL WITH SUPERIOR STRESS CORROSION CRACK RESISTANCE**

(21) Application No.: S54-166413

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SPECIFICATION

1. Title of the Invention

MARAGING STEEL WITH SUPERIOR STRESS CORROSION CRACK RESISTANCE

2. Claims

(1) A maraging steel with superior stress corrosion crack resistance which is comprised of substantially iron remnants and which contains 0.001~ 0.1% total of one kind or two or more kinds of C 0.03% or less, Si 0.1% or less, Mn 0.1% or less, P 0.01% or less, S 0.01% or less, Cu 0.01% or less, Ni 10.0~ 19.0%, Cr 9% or less, Mo 2.0 ~ 20.0%, Co 16.0% or less, Ti 0.1~1.8% , Al 0.5% and Ca or Mg.

(2) A maraging steel with superior stress corrosion crack resistance which is comprised of substantially iron remnants and which contains 0.003~ 0.1% of the total of one kind or two or more kinds of C 0.03% or less, Si 0.1% or less, Mn 0.1% or less, P 0.01% or less, S 0.01% or less, Cu 0.01% or less, Ni 10.0~ 19.0%, Cr 9% or less, Mo 2.0 ~ 20.0%, Co 6.0% or less, Ti 0.1~1.8% , Al 0.5% and Ca or Mg, and rare earth elements.

(3) A maraging steel with superior stress corrosion crack resistance which is comprised of substantially iron remnants and which contains 0.001~ 0.1% of

the total of one kind or two or more kinds of C 0.03% or less, Si 0.1% or less, Mn 0.1% or less, P 0.01% or less, S 0.01% or less, Cu 0.01% or less, Ni 10.0~19.0%, Cr 9% or less, Mo 2.0 ~ 20.0%, Co₁ 6.0% or less, Ti 0.1~1.8% , Al 0.5% and Ca or Mg, and rare earth elements.

3. Detailed Explanation of the Invention

This invention is related to a maraging steel with superior stress corrosion cracking resistance. The maraging steel has a composition which has added an aging hardness element to a high Ni series martensitic steel of extremely low carbon, and by appropriate aging processing, there has been obtained ultra high tensile strength steel with a pull force in excess of 160 Kg/mm². In addition, the same steel, because it has superior notch tenacity compared with other low or intermediate alloy steel, the steel is widely used in products for the aircraft industry, ultra high pressure products, and tool where stability is seen as especially important.

However, there is a problem in that so-called environmental embrittlement is generated in which there is fracturing in a short period of time while using in an environment which contains minute amounts of moisture on the surface, in water or in the air. In order to deal with this problem, there has been much research and many proposals, but there has not been established up to now a sufficient counter measure.

The inventors first sought to obtain a measure for said environmental embrittlement, using existing steel types, and performed detailed electrochemical investigations concerning this environmental embrittlement mechanism, and said embrittlement was not

due to hydrogen embrittlement which was frequently seen for low metal alloy high tension strength steels, and it was determined that the embrittlement was due to active path corrosion which was seen in austenite series stainless steel or copper alloys, that is, it was due to narrowly defined reactive corrosion cracking. Figure 1 shows the relationship of the time required to arrive at fracturing (Hr) and the impressed voltage (mv SCE) when loading (reactive force concentration coefficient Kt) a fixed load (190 Kg/mm²) on the notch base of a notched experimental fragment of general 18% Ni maraging steel (18% Ni- 13% Co- 4% Mo- 1.8% Ti), and when impressing a fixed potential in a normal temperature 0.1 M potassium sulfate (Na₂SO₄) solution. For the time to arrive at fracture, the higher the impressed voltage, the shorter the time, and conversely, the lower the voltage, the more difficult it was to fracture. It was not hydrogen embrittlement that was the cause of this phenomenon, and when there was active path corrosion bending was seen, and it was indicated that the embrittlement of the above-mentioned maraging steel was due to the narrowly defined anti stress corrosion cracking.

The above-mentioned fact was extremely important for the investigation of a countermeasure for environmental embrittlement; and using a means which lowered the material strength which was frequently used as an environmental embrittlement countermeasure for conventional low metal alloy steel high tensile strength steel did not obtain the sought after solution.

The inventors, based on observing the above-mentioned facts, from reactive corrosion experiments done simply in the same way as above, obtained results on the effects of chemical compounds relative to the sensitivity for stress corrosion cracking, and with all

the basic composition series of 12% Ni, 13% Ni and 18% Ni which are the current representative types, by adding a fixed amount of Ti, and by regulating the amount of the impurity Cu and using compositions of Ca and rare earth metals, it was discovered that there would be obtained an improvement in the anti stress corrosion cracking, completing this invention.

That is, this invention using an existing maraging steel composition as a base added Ti approximately 0.1 ~ 1.8%, and Cr approximately 9.0% or less, and along with controlling the Cu impurity to approximately 0.01% or less, was comprised of (a) one kind or 2 kinds of approximately 0.001 ~ 0.1% of Ca or Mg, (b) approximately 0.003 ~ 0.1% of rare earth metals (REM), or (c) a total of 1 kind or two kinds of Ca or Mg and REM as 0.001 ~ 0.1%, and a substantial remnant of iron, which imparted good anti stress corrosion cracking ability, and under every kind of environment, it was possible to stop embrittlement fracturing in water or the atmosphere.

The base composition of this invention contained a component composition of every series of 12% Ni, 13% Ni and 18% Ni as a representative steel kind for maraging steel and was controlled at C 0.03% or less, Si 0.1% or less, Mn 0.1% or less, P 0.01% or less, S 0.01% or less, Cu 0.01% or less, Ni 10.0 ~ 19.0%, Cr 9% or less, Mo 2.0 ~ 20.0%, Co 16.0% or less.

This invention's steel, for the elements which had an important effect on the anti stress corrosion cracking, with respect to the above-mentioned base composition, regulated every component element such as Ti, Cu, Cr and Ca, Mg, REM.

Ti is an indispensable element for the maraging steel as an aging hardening element, and approximately 0.1% is necessary. However, when adding a lot, the sensitivity of the

stress corrosion cracking rose, and especially, when the amount exceeded 1.8%, there was remarkable damage. Accordingly, approximately 1.8% is assumed as an upper limit. Cu is mixed as an impurity element, but its existence has a great effect on the anti stress corrosion cracking ability, and when that amount exceeds 0.01%, the sensitivity increases dramatically. Accordingly, the permissible upper limit is approximately 0.01%.

Cr, instead of an improving effect on general anti-corrosion, heightened the anti stress corrosion cracking ability, and its effect increased along with the added amount. However, if too much was added, notch tenacity suffered, and this chemical was added in a range of 9.0% or less. Moreover, while sufficiently exhibiting the above-mentioned effect, the desirable lower limit was approximately 0.01%.

This invention contains (a) 1 kind or two kinds of Ca and Mg, (b), REM, or (c) 1 kind or two kinds of Ca and Mg with REM, and any group of the 3 groups of (a), (b), and (c). The elements of every group, in addition to the general effect as a deoxidizing agent, played the role to remarkably heighten the anti stress corrosion cracking ability.

The Ca and Mg of the (a) group obtain an improvement effect of identical anti stress corrosion cracking ability, by replacing one element for another using the same effective substances. These elements are added, using the total weight of one or both at 0.001% or more. It is permissible to use each element as the REM of (b) group, but La-Ce are especially appropriate, and addition should be 0.003% or more. In addition the (c) group elements, that when using compounds of every element of the (a) group and the (b) group, there should be additions of 0.001% or more. However, when there is excessive adding of these elements, the improvement effect for anti reactive force corrosion fracturing saturates, and furthermore, there is a lowering of notch tenacity from the increase in non

metal intervening substance amounts. Consequently, a desirable upper limit is approximately 0.1%. Figure 2 is a graph which shows the effect, for a 18% Ni- 13% Co-4% Mo-Ti series maraging steel, of the above-mentioned (a), (b), or (c) group element amount (use La-Ce as REM) with respect to the period (hr) until fracture in the anti stress corrosion cracking experiment. However, for the anti stress corrosion cracking experiment, there was immersion in a 0.1 M -Na₂SO₄ solution (room temperature) of a notched experimental fragment (same figure [I] is the entire body diagram, [II] is expanded diagram of the A part) which was prepared like the form shown in Figure 3, and the notch's base was loaded with a tensile force equivalent to 95% of the notch's tensile strength (reactive force concentration coefficient K_t of the notch part was 3.5), and there was measured the period (hr) until cracking occurred under the same conditions. Moreover, the graph's x-axis shows the total amount of every element of Ca, Mg or REM (however, when adding REM, calculate as 1/3 of said added amount). From the diagram, it was determined that a good anti stress corrosion cracking ability was achieved by adding the amounts at 0.01% or more.

Embodiments

There was prepared a maraging steel for every kind of composition which is shown in Table 1, and after obtaining a steel plate of 1mm thick by performing heat processing and cooling processing under normal conditions, a prescribed solution-aging treatment was executed. From each one of these experimental materials, there was prepared an experimental fragment of a form like that shown in Figure 3 by mechanical processing,

and a stress corrosion cracking experiment was performed under the same conditions as above, and the period until cracking was measured. Moreover, in the first table, the supplied experimental materials (1) ~ (15) were comparative materials, and appropriate amounts of Cr were added to conventional maraging steel. Among (1) ~ (3) there was control of the Cu amount to 0.01% or less. In addition, the supplied materials (4) and (5) had added Ca at 0.003%, and (4) a high Ti amount (1.88%), (5), a high Cu amount (0.021%). On the other hand, supplied experimental materials (6) (15) were the invention's steel (provided that for REM, all used La-Ce). In Table 2 is shown the measurement results (for every supplied experimental material, measurements were made twice). From the same table, Cr was added to the maraging steel, and when the Cu amount was controlled, the anti stress corrosion cracking ability was improved, but when there was an excessive amount of Ti or of Cu, even when adding Ca, an additive effect was not recognized. Accordingly, by adding less than 1.8% Ti, and controlling Cu to 0.01% or less, it was determined that with a maraging steel that appropriately added Ca, Mg, and REM, there could be further improvement in anti stress corrosion cracking ability (supplied experimental material (6) ~ (15)).

Table 1 Experimentally Supplied Chemical Compounds (wt. %)

6	0.010	0.01	0.01	0.005	0.005	12.05	0.018	2.88	0.24	0.17	5.11	0.003	—	—	—	This Invention's Material
7	0.005	0.01	0.01	0.008	0.003	13.12	14.96	9.95	0.18	0.067	0.012	0.002	—	—	—	
8	0.003	0.01	0.01	0.003	0.003	17.89	12.99	4.01	1.36	0.15	0.009	0.005	—	—	—	This Invention's Material
9	0.003	0.01	0.01	0.004	0.002	17.87	13.00	3.93	1.88	0.15	0.010	0.004	0.003	—	—	
10	0.003	0.01	0.01	0.004	0.002	17.84	13.06	3.95	1.38	0.13	0.012	0.021	0.003	—	—	This Invention's Material
11	0.006	0.01	0.01	0.005	0.002	12.11	0.017	2.90	0.23	0.19	5.08	0.003	0.003	—	—	
12	0.004	0.01	0.01	0.005	0.001	18.00	13.12	4.05	1.26	0.10	0.013	0.004	0.001	0.001	—	This Invention's Material
13	0.005	0.01	0.01	0.005	0.001	18.01	13.07	3.98	1.60	0.14	0.015	0.005	—	0.05	—	
14	0.004	0.01	0.01	0.005	0.001	18.03	13.00	4.02	1.32	0.09	0.017	0.007	—	—	0.008	This Invention's Material
15	0.003	0.01	0.01	0.004	0.002	17.96	12.97	3.96	1.70	0.11	0.016	0.002	0.001	0.001	0.002	
16	0.005	0.01	0.01	0.006	0.001	18.12	12.94	4.03	0.88	0.14	0.014	0.002	0.03	—	—	This Invention's Material
17	0.004	0.01	0.01	0.005	0.002	17.97	13.04	4.05	0.36	0.16	0.010	0.004	—	0.002	0.003	
18	0.007	0.01	0.01	0.004	0.001	18.10	11.97	3.99	1.22	0.13	1.04	0.001	0.002	—	—	This Invention's Material
19	0.005	0.01	0.01	0.004	0.004	14.68	12.30	4.02	1.44	0.08	2.88	0.002	0.005	—	—	
20	0.006	0.01	0.01	0.004	0.002	11.21	12.80	3.96	1.58	0.06	8.41	0.003	0.003	—	—	This Invention's Material

Table 2 Measurement Results

	Time Till Cracking		
1	300 ,	180	Comparative Material
2	58 ,	240	
3	400 ,	450	
4	200 ,	320	
5	150 ,	167	
6	> 500 ,	> 500	
7	> 500 ,	> 500	
8	> 500 ,	> 500	
9	> 500 ,	> 500	
10	> 500 ,	> 500	
11			This Invention's Material
12			
13			
14			
15			

As shown in Table 2, this invention's steel exceeded 500 hours for all material before cracking, and compared to the conventional maraging steel, it was determined that the anti stress corrosion cracking ability was of a stabilized high level.

In this way, this invention's steel even in water or in the atmosphere, does not generate environmental embrittlement which cracks in a short period of time like conventional materials, and because this material property is maintained over a long period of time, with which respect to every kind of use such as in aircraft parts which require a high °C of stability as well as tensile strength, it is possible to supply a highly reliable material.

4. Brief Explanation of the Drawings

Figure 1 is a graph which shows the effect of added potential on the lifetime of the stress corrosion cracking ability of the maraging steel of the 18% Ni- 13% Co – 4% Mo- 1.8% Ti series, and Figure 2 is a graph which shows the effect of added elements on the lifetime of the anti stress corrosion cracking ability of maraging steel of the 18% Ni-13% Co- 4% Mo- Ti series, and Figure 3 [I] is a diagram which shows the shape of an experimental fragment which is used for the stress corrosion cracking ability experiment and Figure 3 [II] is an expanded diagram of the A part.

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